

*Univ. of Houston*  
*NSG-257-62*

N 63 17157

**ULTRA-VIOLET-ABSORBING  
COMPOUND(S) REPORTED PRESENT  
IN THE MURRAY METEORITE**

By

**Prof. J. ORÓ**

*(Reprinted from Nature, Vol. 197, No. 4869, pp. 756-758,  
February 23, 1963)*

## ULTRA-VIOLET-ABSORBING COMPOUND(S) REPORTED PRESENT IN THE MURRAY METEORITE

By PROF. J. ORÓ

Lawrence Radiation Laboratory, University of California,  
Berkeley, California, and Chemistry Department, University of  
Houston, Texas

**P**RELIMINARY investigations<sup>1-9</sup> have shown that when a water extract of the Murray meteorite is applied to a column of 'Dowex 1' resin and eluted with water or with 0.05 N hydrochloric acid, the eluates contain ultra-violet-absorbing compound(s).

Since some ion-exchange resins are known to yield water-soluble ultra-violet-absorbing substances<sup>10</sup> the investigations reported here were undertaken to ascertain whether the compounds detected in meteorite extracts are indigenous to the meteorite or are the result of contamination by the analytical technique used. These show that the ultra-violet spectra obtained from meteorite extracts passed through 'Dowex 1' and the spectra given by blank eluates from 'Dowex 1' are essentially identical. Observations concerning the presence of similar water-soluble ultra-violet-absorbing substances in 'Dowex 2' resin are also described.

The observations made by Vaughn<sup>1-4</sup> on the water extract from the Murray meteorite can be summarized as follows:

(1) The spectrum obtained directly with the water extract of the meteorite showed no maxima in the ultra-violet region. A uniform absorption at the short wavelength end of the spectrum and a very weak shoulder in the 260-280 m $\mu$  region were only observed<sup>1,2</sup>.

(2) No peak was found in the ultra-violet spectrum of the distillate obtained at 300° C in vacuum from the dry residue of the water extract<sup>1</sup>.

(3) ~~When the water extract was applied to a 'Dowex 1' column and the column eluted first with water and then with 0.05 N hydrochloric acid, a small amount of ultra-violet-absorbing material was observed to emerge with the water eluate and a larger amount with the acid eluate.~~

(4) The ultra-violet-absorbing spectra of the eluates, in particular of the acid eluate rechromatographed a second time through 'Dowex 1', showed at pH 2 two absorption peaks: a strong one with a maximum at about 230 m $\mu$ .

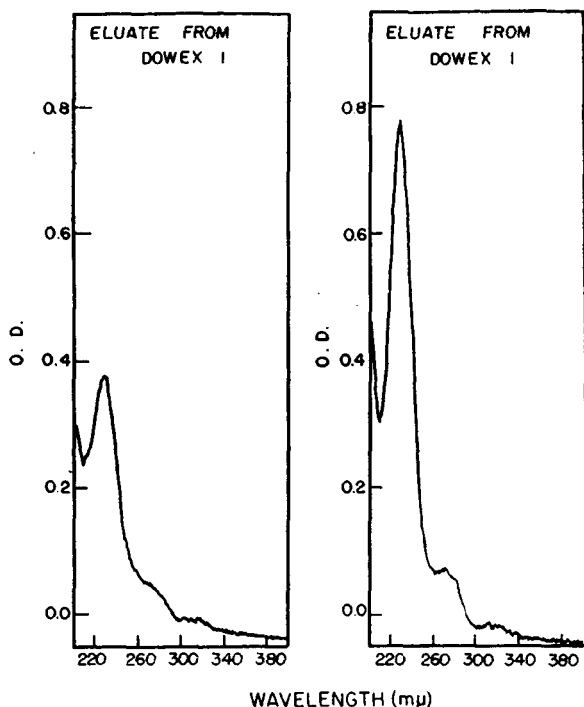


Fig. 1. Ultra-violet absorption spectra of blank eluates from columns of 'Dowex 1' resin (Cl<sup>-</sup> form). The eluates were obtained with 0.1 N hydrochloric acid at room temperature (left) and at 90° C. (right)

and a smaller one with a maximum at about 273 mμ (refs. 2 and 3) (the maxima from the water eluate and from the first acid eluate were less well defined, yet in agreement with the above maxima).

(5) At neutrality and under basic conditions (pH 9–10) the 230 mμ maximum shifted towards shorter wave-lengths (about 222 mμ) while the 273 mμ maximum was very much decreased and in some cases disappeared.

(6) The ultra-violet spectrum in the region 290–250 mμ, observed in CCl<sub>4</sub> and benzene extracts of the meteorite, was found to be caused by the presence of elemental sulphur<sup>2</sup>.

The 'Dowex 1' ion-exchange resin which I used was obtained from a source identical to that of the resin that had been used previously in the meteorite investigations.

A small column (5 c.c.) of 'Dowex 1' (200–400 mesh, × 8, Cl<sup>-</sup> form) was eluted with 10 ml. 0.1 N hydrochloric acid at room temperature. The ultra-violet spectrum of the eluate was recorded in a Cary spectrophotometer (Fig. 1, left). Alternatively, an acid eluate of the same

# ELUATE FROM DOWEX I

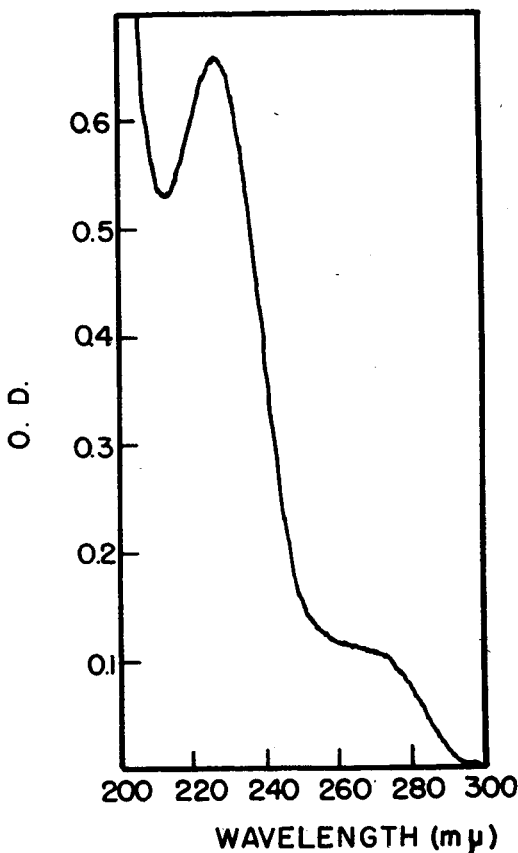


Fig. 2. Ultra-violet spectrum of a 0.1 N hydrochloric acid eluate from a column of 'Dowex 1' resin. The resin has been extracted previously with ether, treated with saturated sodium bicarbonate and washed with distilled water. (Data provided by Dr. J. Ullrich)

resin was obtained by passing 10 ml. of hot (90° C) 0.1 N hydrochloric acid through a small column (1 c.c.) of 'Dowex 1'. The ultra-violet spectrum of the eluate is shown in Fig. 1 (right). A strong absorption peak at about 230 mμ and a smaller one at about 273 mμ can be observed in the two spectra.

The relatively larger ultra-violet absorption of the eluate obtained at 90° C compared with that obtained at room temperature indicates that the extraction of the ultra-violet-absorbing material from the resin is enhanced by the hot acid.

# ELUATE FROM DOWEX 2

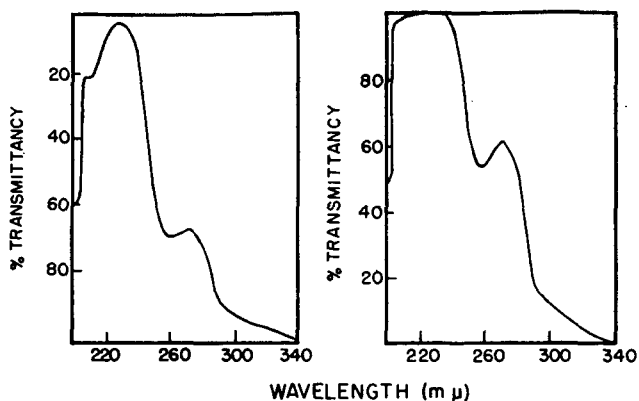


Fig. 3. Ultra-violet absorption spectra of a 4 N acetic acid eluate from a column of 'Dowex 2' resin (OH<sup>-</sup> form). The acetic acid was evaporated and the residue dissolved in 0.1 N hydrochloric acid. (Spectra obtained by L. Engberg)

Elution of the same ultra-violet-absorbing material was also observed from samples of resin which were extracted with ether, regenerated with saturated sodium bicarbonate, washed with distilled water and finally eluted with 0.1 N hydrochloric acid. Fig. 2 shows the spectrum of one such eluate. The fact that this ultra-violet-absorbing material is present after regeneration of the resin indicates that the ultra-violet-absorbing compounds are released from the inside of the resin beads. This observation is also in line with the results obtained in the extraction with hot acid.

Since 'Dowex 2' ion-exchange resin might be used in similar analytical applications, the presence of ultra-violet-absorbing compounds in the acid eluates from this resin was also examined.

A small column (5 c.c.) of 'Dowex 2' (200-400 mesh,  $\times 8$ , OH<sup>-</sup> form) was eluted with 10 ml. of 4 N acetic acid. After evaporation of the acetic acid the residue was dissolved in 0.1 N hydrochloric acid. Fig. 3 shows two of the typical spectra obtained from a number of 'Dowex 2' acetic acid eluates by this procedure. The same two absorption peaks at about 230 and 273 m $\mu$  can be observed.

The identity of the absorption peaks obtained from resins of type 1 and type 2 is not surprising. In fact, it should be expected since these two types of resins have the same structural polystyrene backbone and are manufactured following essentially the same procedure<sup>11</sup>.

The effect of pH change on the ultra-violet absorption curve of a hydrochloric acid eluate from 'Dowex 2' is

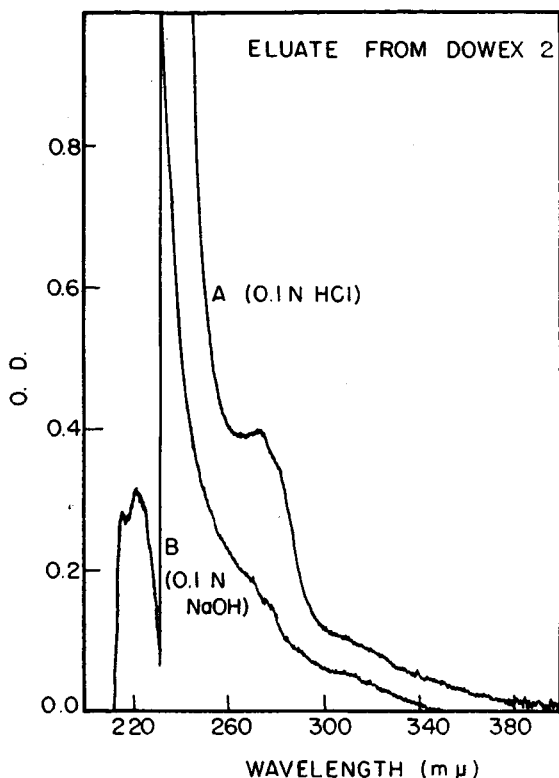


Fig. 4. Spectrum of a 0.1 N hydrochloric acid eluate from a column of 'Dowex 2' resin (curve A) and spectrum of the same eluate after it was made 0.1 N basic with sodium hydroxide (curve B)

shown in Fig. 4. Curve A shows the ultra-violet absorption of the 0.1 N hydrochloric acid eluate, whereas curve B shows the ultra-violet absorption of the same eluate after it was made 0.1 N basic with sodium hydroxide. It can be seen that in 0.1 N sodium hydroxide the 273 mμ absorption peak disappeared and the 230 mμ maximum was shifted to about 222 mμ. These changes are identical to those observed by Vaughn with the 'Dowex 1' eluates of a water extract of the Murray meteorite<sup>2</sup>.

When 'Dowex 2' (OH<sup>-</sup> form) columns were eluted with water and then with 4 N acetic acid the ultra-violet-absorbing material was found in the water eluates as well as in the acid eluates, thus paralleling also the elution behaviour described for the meteorite extracts.

On the basis of the identity of the maxima, identity of shifts caused by changes in pH and similarity of elution pattern (observations 4, 5 and 3 of Vaughn, respectively) it is concluded that the ultra-violet-absorbing compound(s)

detected in water extracts of the Murray meteorite after treatment with 'Dowex 1' came from the resin and not from the meteorite. This conclusion is also in line with the other observations made by Vaughn<sup>1,2</sup>.

These results do not exclude the possibility that some ultra-violet-absorbing substances, other than elemental sulphur, are present in the Murray meteorite in amounts below the limit of detectability by the procedure used by Vaughn. The very weak shoulder observed in the 260–280 m $\mu$  region in the water extracts may be indigenous to the meteorite or may be due to contamination from organic solvents (benzene, etc.) with which the meteorite samples were extracted prior to the extraction with water. Analysis of the Murray meteorite using more sensitive spectrophotometric methods is in progress.

I thank Prof. M. Calvin for providing the laboratory facilities and the stimulus to carry out this work. The data provided by J. Ullrich and L. Engberg are also gratefully acknowledged.

This work was sponsored in part by the U.S. Atomic Energy Commission and by a grant (NsG 257-62) from the National Aeronautics and Space Administration.

<sup>1</sup> Vaughn, S. K., in *Bio-Organic Chemistry Quart. Rep.*, UCRL-8961, **44** (Sept. 1959).

<sup>2</sup> Vaughn, S. K., in *Bio-Organic Chemistry Quart. Rep.*, UCRL-9041, **24** (Dec. 1959).

<sup>3</sup> Himes, S. V., (née Vaughn) in *Bio-Organic Chemistry Quart. Rep.*, UCRL-9208 **7**, (March 1960).

<sup>4</sup> Himes, S. V., in *Bio-Organic Chemistry Quart. Rep.*, UCRL-9772, **1**, (June, 1961).

<sup>5</sup> Calvin, M. and Vaughn, S. K., in *Proc. First Space Sci. Symp.*, Nice, France, 1960, 1171 (North Holland Publ. Co., Amsterdam, 1960).

<sup>6</sup> Calvin, M., *Chem. Eng. News*, **39**, (21) 96 (1961).

<sup>7</sup> Calvin, M., *Ann. Intern. Med.*, **54**, 954 (1961).

<sup>8</sup> Calvin, M., *Chemical Evolution* (University of Oregon Books, Eugene, Oregon, 1961).

<sup>9</sup> Calvin, M., *Perspec. Biol. Med.*, **5**, 399 (1962).

<sup>10</sup> Schwartz, D. (private communication, Berkeley, 1962).

<sup>11</sup> Kressman, T. R. E., in *Ion Exchangers in Organic and Biochemistry*, edit. by Calmon, C., and Kressman, T. R. E., **3** (Interscience Publishers, New York, 1957). See also, *Dowex: ION Exchange*, **4** (The Dow Chemical Co., Midland, Mich., 1958).